

Contribution from the Chemical Laboratory, Presidency College, Calcutta.
On Double Thiosulphates of Copper and Sodium.—By CHANDRA
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 PREM CHAND ROYCHAND SCHOLAR. Communicated by ALEX. PEDLER,
 F.R.S.

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When working with the preparation of a few normal sulphites and particularly during an attempt to prepare normal cuprous and cupric sulphites, we had occasionally to use sodium thiosulphate instead of sodium sulphite or sulphur dioxide dissolved in water. It was soon found that a beautiful yellow salt separates, on allowing a mixture of sodium thiosulphate and copper sulphate solutions to stand for some time, in microscopic needles which however decomposes readily in a day or two unless special care is taken to get it perfectly dry. By varying the concentration and proportion, with or without addition of alcohol, the colour of the salts obtained seemed to change considerably. We undertook to analyse some of them, and the result of the analyses forms the subject matter of the present paper.

But before proceeding to describe our work a brief notice of the work done by previous chemists on the subject may not be out of place. The following list includes all the salts known at present.

Cuprous Sodium thiosulphate:—

- (1) $2 \text{Cu}_2\text{S}_2\text{O}_3 \cdot 7 \text{Na}_2\text{S}_2\text{O}_3 \cdot 2 \text{H}_2\text{O}$ (Jochum C. C. 1885, 642).
- (2) $2 \text{Cu}_2\text{S}_2\text{O}_3 \cdot 7 \text{Na}_2\text{S}_2\text{O}_3 \cdot 12 \text{H}_2\text{O}$ (Jochum).
- (3) $\text{Cu}_2\text{S}_2\text{O}_3 \cdot 3 \text{Na}_2\text{S}_2\text{O}_3 \cdot 2 \text{H}_2\text{O}$ (Rammelsberg Pogg. 56, 321).
- (4) $\text{Cu}_2\text{S}_2\text{O}_3 \cdot 3 \text{Na}_2\text{S}_2\text{O}_3 \cdot 6 \text{H}_2\text{O}$ (Jochum).
- (5) $3 \text{Cu}_2\text{S}_2\text{O}_3 \cdot 2 \text{Na}_2\text{S}_2\text{O}_3 \cdot 8 \text{H}_2\text{O}$ (Vortmann, M. Ch. 9, 165).
- (6) $3 \text{Cu}_2\text{S}_2\text{O}_3 \cdot 2 \text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ (Lenz. A. 40, 99).
- (7) $5 \text{Cu}_2\text{S}_2\text{O}_3 \cdot 4 \text{Na}_2\text{S}_2\text{O}_3 \cdot 8 \text{H}_2\text{O}$ (Jochum).
- (8) $5 \text{Cu}_2\text{S}_2\text{O}_3 \cdot 4 \text{Na}_2\text{S}_2\text{O}_3 \cdot 6 \text{H}_2\text{O}$ (Jochum).
- (9) $\text{Cu}_2\text{S}_2\text{O}_3 \cdot \text{Na}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Russel Ch. Ztg. 9, 233).
- (10) $\text{Cu}_2\text{S}_2\text{O}_3 \cdot \text{Na}_2\text{S}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$ (Vortmann M. Ch. 9, 165).
- (11) $5 \text{Cu}_2\text{S}_2\text{O}_3 \cdot 3 \text{Na}_2\text{S}_2\text{O}_3 \cdot 2 \text{Na}_4\text{SO}_4 \cdot \text{H}_2\text{O}$ (Jochum).

Cuprous Sodium thiosulphate Cupric Sulphide :—

(1) $\text{Cu}_2\text{S}_2\text{O}_3 \cdot \text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Cu S} \cdot 4\text{H}_2\text{O}$ (Lenz. A. 40, 99).

(2) $\text{Cu}_2\text{S}_2\text{O}_3 \cdot \text{Na}_2\text{S}_2\text{O}_3 \cdot 2\text{Cu S}$ (Kessel B. 11, 1585).

Cuprous Sodium thiosulphate Sodium Chloride :—

$3\text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3 \cdot 4\text{Na Cl} \cdot 8\text{H}_2\text{O}$ (Siewert, Zeit. ges. Naturwiss. 26, 486).

Cuprous thiosulphate sodium dithionate :—

(1) $\text{Cu}_2\text{S}_2\text{O}_3 \cdot 4\text{Na}_2\text{S}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ (Vortmann).

(2) $2\text{Cu}_2\text{S}_2\text{O}_3 \cdot \text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{Na}_2\text{O}$ (Jochum).

See Dictionary of Chemical Solubilities, Inorganic by A. M. Comey, 1896, page 474, and Dammer's Handbook II, 2 pages, 688-89.

The yellow salt to which Lenz and Siewert assigned the formula $\text{Cu}_2\text{S}_2\text{O}_3 \cdot \text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Cu S} \cdot 4\text{H}_2\text{O}$, was found by Kessel to have the above composition when prepared at 10°C , and to vary in composition with variation of temperature. Kessel further noticed that the yellow salt is obtained when the copper sulphate and sodium thiosulphate are mixed in the proportion of one molecule of the former to two molecules of the latter. He further says that the reaction takes place in two stages. According to him the yellow salt is decomposed by cold strong hydrochloric acid forming a white mass which contains neither free sulphur nor copper chloride, is permanent when dry, but in contact with moisture decomposes with separation of copper sulphide and evolution of sulphur dioxide. He is, however, of opinion that the sodium chloride is present as an impurity having had nothing to do with the composition.

Vortmann on the other hand, disagreeing with Kessel describes two salts, one a greenish yellow salt $\text{Cu}_2\text{S}_2\text{O}_3 \cdot \text{Na}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and the other an intense citron yellow salt $3\text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$. The former according to him is obtained in microscopic needles when saturated solutions of copper sulphate and sodium thiosulphate are mixed together in the proportion of one molecule of the former to two molecules of the latter. When, however, the solutions are previously heated to about 40°C and then mixed together, the temperature of the mixture rises about 5° — 7° and the salt with the composition $3\text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ separates out, also in microscopic needles. The yellow salt is unstable and decomposes thus— $3\text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3 \cdot 8\text{H}_2\text{O} = 3\text{Cu}_2\text{S} + 2\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + \text{S}_2 + 2\text{SO}_2 + 7\text{H}_2\text{O}$.

The salt we are going to describe agrees in some respects with the yellow salt described by Lenz and Siewert and confirmed by Kessel, as also with that described by Vortmann. That there should be copper sulphide present in a salt with such an intense yellow colour seemed to us strange. This led us to analyse the salt once again. To start with,

it was found that the same yellow salt is invariably obtained at all temperatures between 20°C and 34°C provided the green colour of the mixture is not discharged by an excess of sodium thiosulphate. Even with fairly dilute solution, the same salt is obtained. In one or two cases, however, the sodium thiosulphate was so much in excess that the liquor left after the separation of the crystals was yellow. Sometimes the precipitate was allowed to remain in contact with the mother liquor overnight. It may be mentioned here that the salt separates out soon when prepared from concentrated solutions. If, however, dilute solutions are used it takes a much longer time for the salt to crystallise out, but it is richer in colour and more distinct in crystalline structure. In contact with the mother liquor decomposition sets in generally after a day or two, and a dark reddish brown precipitate, more soluble in water than the yellow salt, is formed which finally changes into black insoluble copper sulphide, the supernatant liquid becoming perfectly clear and transparent. In the first few preparations the salt was simply washed with water, in which it seemed to dissolve to a slight extent, until free from sulphuric acid, pressed between filter paper, powdered and dried by exposure to the air. It was found, however, that the salt so treated did not keep well for a few days, decomposition setting in, sometimes, even in course of a few hours. The colour slowly changed to black, and sulphur dioxide was evolved. It was subsequently found that a fairly stable salt could be obtained if it were washed at first with water until free from sulphuric acid and finally repeatedly with rectified spirit over filter pump, dried by exposure to the air, powdered, and carefully sifted in a fine sieve. The salt thus prepared did but lose a triffing when kept in a desiccator over calcium chloride for weeks together. The result of a determination of the loss is given here using about (7) seven grams of the salt.

22nd December, 1896. Platinum basin and salt = 31·2436 grams.

23rd	„	„	„	= 31·2425	„
9th	January,	1897.	„	= 31·2412	„
26th	„	„	„	= 31·2412	„

Thus about 7 grams of the salt lost only 2·5 milligrams in three weeks. This loss may easily be accounted for from a small quantity of alcohol still present in the air dried sample. In connection with the decomposition of this salt at ordinary temperature, it may conveniently be pointed out, here, that more dense the precipitate is and the richer the colour, the better it keeps. Moisture is perhaps the most important factor in bringing about the decomposition, as appears from a little of the above sample, kept sealed in an ordinary glass tube. While the substance kept quite well in a desiccator over calcium chloride for about

a month, the salt in the sealed tube began to change in the course of a few days. It is also important to mention here that the salt does not keep in contact with alcohol as was often noticed during specific gravity determination. Alcohol therefore appears to have a twofold action when used in washing the moist salt. Firstly, owing to its strong affinity for water, it removes easily the last trace of moisture from the salt, and secondly being in itself very volatile entirely disappears when exposed to the air.

A series of analysis was made with samples prepared on different occasions under varying conditions, and the result is tabulated on next page.

From the percentage composition we obtain the following atomic ratio:—

$$\begin{aligned} \text{Cu : Na : S : O} &= \cdot 514 : \cdot 369 : \cdot 874 : 1\cdot 984 \\ &= 1\cdot 4 : 1 : 2\cdot 4 : 5\cdot 5 \\ &= 7 : 5 : 12 : 27\cdot 5 \end{aligned}$$

The composition obtained from the analysis of different samples agree so well among one another that there is no reason to assume it to be a mixture. On the contrary it may fairly be assumed to be a compound with definite composition. It has also been found that different crops of the salt obtained from the same mixture at different intervals have identical composition (see samples B. 1 and B. 2).

On adding caustic soda to a mixture of cupric sulphate and sodium thiosulphate, a blue precipitate is obtained indicating the presence of bivalent copper. If, however, the caustic soda is added after some time when the formation of the yellow salt begins, the yellowish red cuprous hydrate is obtained. On adding caustic soda to the yellow salt suspended in water, the latter is decomposed, and the same reddish yellow cuprous hydrate is obtained. This indicates that the first stage of the reaction consists in the reduction of the cupric copper to cuprous copper, and it is during the second stage that the precipitation of the yellow salt commences. The formation of the yellow salt is neither sudden nor rapid, one or two days being sometimes necessary for complete precipitation. It appears as probable that a portion of the copper in solution undergoes oxidation with the reformation of copper sulphate and reproduction of a blue solution.

The salt thus prepared was subjected to a careful qualitative analysis for all other possible sulphur compounds, as for instance sulphuric acid both free and combined, a sulphide, a sulphite, and the thionates. It was found, however, that none of these compounds are present in the salt even as an impurity. But it gave all the reactions

Table of Analysis of the yellow salt obtained by the action of sodium thiosulphate on copper sulphate or acetate.
(Temperatures 20°–35°C).

Date of preparation.	Sample number.	Weight in grains of substance used.	Weight in grains of Cu_2S .	Weight in grains of Na_2SO_4 .	Weight in grains of BaSO_4 .	Weight in grains of Ag Br.	Weight in grains of H_2O .	PERCENTAGE OF					ATOMIC RATIO OF					REMARKS.
								Cu.	Na.	S.	O.	H_2O .	Cu.	Na.	S.	O.	H_2O	
Oct. 5, 1896	A.1.	0.4923	0.2016	...	1.0025	32.68	...	27.98	Beautiful yellow colour.	
		0.5094	0.2092	...	1.0422	32.77	...	28.12		
		0.7652	0.3118	32.76		
Oct. 20, 1896	A.2.	0.7230	0.2958	...	1.4762	32.67	...	28.00	Slightly decomposed and slight smell of SO_2 . Water estimated at about 240°C.		
		0.3474	2.5883	31.73	
		0.6323	0.0580	9.2	
Oct. 23, 1896		0.5556	0.2290	0.1448	32.71	8.68	Slightly decomposed and slight smell of SO_2 . Water estimated at about 240°C.		
Oct. 30, 1896	A.3.	0.5254	0.2150	0.1376	0.0493	32.65	8.48	9.38			
		0.2767	2.0688	31.84	
		0.3993	0.8128	27.99	5.16	3.69	8.79	1.99	5.23	
		0.9535	0.0904	9.46		
Nov. 11, 1896	A.4	0.759	0.3112	0.1985	32.72	8.47	Slightly discoloured.		
		0.406	3.0197	31.67			
		0.2941	0.5969	27.9			
		1.032	0.4235	32.75		5.17	3.69

of thiosulphuric acid. Hence it was concluded that the substance was a double thiosulphate of copper and sodium, and we confirmed it by quantitative estimation of the acid. We estimated the thiosulphuric acid both by the direct action of iodine on the salt acidulated with hydrochloric acid, and by decomposing the salt with caustic soda, filtering and titrating the filtrate by iodine after acidification. The results are tabulated below:—

1 c.c. IODINE SOLUTION = 0.1516 GRAM I. = 0.1365 GRAM $H_2S_2O_3$.

A.

Table of direct titration with iodine solution.

Wt. of Salt used (Sample VII).	Vol. of Thio- sulphate required.	Vol. of Thio. calculated for 1 gr. Salt.	Mean.	Percentage of $H_2S_2O_3$.
0.2909 gram.	10.6 c. c.	36.6 c. c.		
0.1880 „	6.9 c. c.	36.7 c. c.	36.63	50
0.3467 „	12.7 c. c.	36.6 c. c.		

B.

Table of titration of the filtrate after decomposing the salt by NaOH and filtration.

Wt. of Salt used.	Vol. of Thio- sulphate required.	Vol. of Thio. calculated for 1 gr. Salt.	Mean.	Percentage of $H_2S_2O_3$.
Sample VII. {	1.0637 gram.	38.25 c. c.	36. c. c.	
	1.5558 „	53.5 c. c.	36.3 c. c.	
			36.2	49.3
0.6190 „	22.0 c. c.	36.3 c. c.		
1.9320 „	67.9 c. c.	35.1 c. c.*		

On comparing the two tables it is found that the result of table A is slightly higher than that of B. The total sulphur 27.95% if calculated as thiosulphuric acid would give 49.8%; so that there is fair agreement between the calculated result and that obtained by the

* In this case the result is too low as the salt was slightly decomposed and discoloured.

method A. This proves that the whole of the copper is present in the cuprous state, otherwise the iodine required for direct titration would be less, owing to the liberation of iodine by the cupric salt from potassium iodide. The little discrepancy between A and B will be explained later on.

Another important point should be mentioned here in connection with the determination of water. It will be seen on going through the table that when the water is estimated by heating the substance at temperatures up to 250° C. in a current of carbon dioxide and causing the sulphur dioxide evolved to be absorbed by lead dioxide, we get 9.46 % of water. On the other hand when it is heated rather strongly and the evolved sulphur dioxide is absorbed by red hot lead chromate, the result is 10.5 % . It was further noticed that the major portion of the water was liberated before the evolution of any considerable amount of sulphur dioxide began. During the decomposition of the salt a small quantity of sulphuric acid is formed which with the sodium sulphate, another product of decomposition, may form sodium hydrogen sulphate, thus accounting for the increased percentage of water at a very high temperature. We propose to take up the subject in a future communication in connection with the decomposition of the salt.

It may hence be concluded that the substance is a double thio-sulphate of copper and sodium having the formula $7 \text{Cu}_2\text{S}_2\text{O}_3 \cdot 5 \text{Na}_2\text{S}_2\text{O}_3 \cdot 16 \text{H}_2\text{O}$ with the following percentage composition:—

Copper = 32.24 %.		= 27.95 %.
Sulphur = 8.37 %.	Oxygen (for complete oxidation) = 32.05 %.	
Water = 10.48 %.		

The salt with the composition as given above should however take 32.04 % oxygen for complete oxidation of the salt to copper sulphate and sodium sulphate. There seems to be a slight difference between the calculated percentage of oxygen and that obtained as a mean of several analysis. This difference however disappears if the result of the analysis of the last preparation, the most stable in the batch, is considered.

V. Hauer says that an acid cuprous thio-sulphate of the formula $\text{Cu}_2\text{H}_4 (\text{S}_2\text{O}_3)_3$ may be obtained by adding a concentrated solution of copper sulphate to a strong solution of sodium thio-sulphate until the colour is deep yellow and gently heating the mixture, as yellow prismatic crystals. We have repeatedly tried to prepare the salt, but as often have we failed. The crystals obtained, invariably contained sodium thio-sulphate, and when the heating was carried beyond 35-40°C. the mixture in some cases changed colour from yellow to a dark reddish

brown in the course of a few minutes, and finally deposited a dark-brown precipitate readily soluble in water. If, however, thoroughly saturated solutions of both copper sulphate and sodium thiosulphate, previously heated to about 50-60°C., be used, similar yellow crystalline precipitate is obtained which settles down easily. Care should however be taken in washing the salt, as a comparatively large quantity of sodium sulphate is formed in this case which has to be removed. But the freshly precipitated salt is also sensibly soluble in water. It should therefore be drained as completely as possible, washed once or twice with water and then with dilute alcohol gradually increasing the strength of alcohol and finally with alcohol alone. Different samples have been thus prepared with slight modification in the process, and the result of the analysis of the same are included in the annexed table. On examination it will however be found that although the samples appear to be identical in physical properties, they all differ more or less in composition and that therefore different formulæ should be given to them. (See Table p. 243).

As we had reason to believe that the percentage of sodium in F was a little too high the atomic ratio appears to be as Cu : Na : S : O : H₂O = 4 : 3 : 7 : 16 : 6 corresponding to the formula 4 Cu₂ S₂ O₃, 3 Na₂ S₂ O₃ 9 H₂O. With the following percentage composition:—

$$\begin{array}{ll} \text{Cu} = 31.84 \% & \text{S} = 28.17 \% \\ \text{Na} = 8.68 \% & \text{O} = 32.20 \% \end{array} \quad \text{H}_2\text{O} = 10.2 \%$$

In E the ratio of copper to sodium is as 7 : 6.

By heating therefore with sodium thiosulphate a part of copper is separated, thus increasing the percentage of sodium and sulphur. But whether at any particular temperature a compound of perfect definite composition is formed or not, it is impossible to say positively.

We next proceeded to consider what takes place when copper acetate is used instead of copper sulphate, thinking that acetic acid being a weaker acid might give the normal copper thiosulphate or the acid salt of V. Hauer. Copper acetate is less soluble in water than copper sulphate, and accordingly we had to work with comparatively dilute solutions. Thinking that concentration and relative proportion might produce corresponding difference in composition standard solutions of copper acetate and sodium thiosulphate (1 c.c. Thio. = 10.835. $\frac{N}{10}$ Thio. = 10.835 × .0248 gms. Thio. = .2687 gms. and 1 c.c. copper acetate = .0182 gms. Cu) were prepared. Kessel and Vortmann state that the yellow salt described by them can only be obtained when the two solutions are mixed in the ratio of one molecule of copper salt to two

Table of analysis of the yellow salt obtained by the action of a strong solution of sodium thiosulphate on a saturated solution of copper sulphate at temperatures from 40°C–70°C.

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Date.	Sample.	Weight in grams of substance taken.	Weight in grams of Cu_2S .	Weight in grams of Na_2SO_4 .	Weight in grams of BaSO_4 .	Weight in grams of Ag Br .	Weight in grams of H_2O .	PERCENTAGE OF					REMARKS.	
								Cu.	Na.	S.	O.	H_2O .		
March 24, 1897.	E.	0.9581	0.3738	0.2854	0.101	31.3	9.51	10.54	Temperature of preparation 50–60°C. Water determined at 150–160°C.	
		1.2344	0.4788	0.3700	0.1274	30.95	9.71	10.33		Water determined at 190–200°C.
		1.2108	0.4720	0.3634	0.1260	31.1	9.72	10.4		
		Mean.						31.12	9.65	10.42		
	F. 1.	0.9429	0.3739	0.2603	31.5	8.96	Temperature of preparation 60–70°C.	
		0.5408	4.0700	32.04	...		
		1.1134	0.1216	10.92		
		0.9234	0.3666	...	1.8922	31.68	...	28.14		
		F. 2.	0.6232	0.3174	...	1.284	31.66	...	28.3
			0.7960	...	0.2233	9.12
	Mean.						31.61	9.04	28.22	32.04	10.92			

molecules of sodium thiosulphate. It was soon found that no precipitate is obtained when the mixture is made in the ratio of one molecule of the copper salt to two molecules of the sodium salt, and that the same yellow salt is obtained when they are mixed in any other proportion less than the above.

When the yellow salt is treated with a solution of sodium hydrate, an orange coloured precipitate of cuprous hydrate is obtained. If, however, the precipitation is effected in presence of a large volume of water the bright reddish yellow dense precipitate becomes voluminous, turns dirty brown and can easily be filtered. From concentrated solution the whole of the copper cannot be completely precipitated and separated, a portion invariably going into solution. The light brown precipitate after being thoroughly washed, dissolves in dilute hydrochloric acid; a small quantity possessing a black colour however remain undissolved. No sulphur free or combined can be detected in the solution. The insoluble residue can only be dissolved in aqua regia and on analysis was found to contain copper and sulphur only. The residue therefore consists of copper sulphide. It becomes now of importance to decide whether the sulphide is present as such in a soluble form in the original salt or that it is a product of a secondary reaction. We are of opinion that the latter supposition is the correct one and we shall presently give reasons for it.

As already stated the bright orange red precipitate cannot be filtered easily. If, however, the mixture be very gently heated, the precipitate settles down easily and can therefore be filtered readily. Should it however be heated nearly to boiling the precipitate darkens in colour. The residue after careful washing, on treatment with dilute hydrochloric acid leaves a considerably greater quantity of the black copper sulphide than that obtained in the cold. It is therefore clear that the sulphide of copper which is found along with cuprous hydrate is a product of a secondary reaction between sodium thiosulphate and cuprous hydrate. That this is the true explanation of it will be evident from the following consideration. Sodium thiosulphate is neutral to test paper; so also is cuprous hydrate or oxide. But when cuprous oxide is treated with a solution of sodium thiosulphate, a strongly alkaline liquid is obtained even in the cold. According to Field (*Quarterly Journal of the Chemical Society* xvi. 28.) cuprous hydrate dissolves in sodium thiosulphate solution at the ordinary temperature and is reprecipitated on heating. We found, however, that with the application of heat a considerably greater quantity of cuprous hydrate dissolves. To examine this reaction quantitatively weighed quantities of cuprous oxide containing 98.5% of real cuprous oxide were dissolved in excess

of sodium thiosulphate with the application of gentle heat and the sodium hydrate produced was estimated by standard acid, using phenolphthaliene as an indicator. The result is tabulated below:—

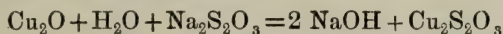
Weight of Cu_2O used.	Vol. of standard hydrochloric acid used.	Vol. of the standard hydrochloric acid required for 1 gram of the oxide.	Mean.
0·3162 grams.	21·7 c.c.	68·6 c.c.	68·8 c.c.
0·2558 "	17·4 c.c.	68·4 c.c.	
0·2928 "	20·3 c.c.	69·3 c.c.	
0·2539 "	17·5 c.c.	68·92 c.c.	
1·7688 "	121·9 c.c.	68·94 c.c.	

1 c.c. of the standard acid used contained 0·00734 gram of true hydrochloric acid gas.

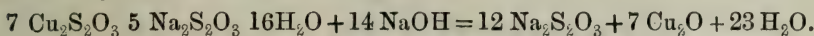
∴ 0·985 grams of real cuprous oxide liberated a quantity of caustic soda which required 68·8 c.c. of the standard acid or one gram of real cuprous oxide liberates $\frac{68\cdot8 \times 0\cdot00734 \times 40}{36\cdot5 \times 985} = 0\cdot562$ grams of caustic soda.

$$\begin{aligned} \therefore \text{Cu}_2\text{O} : \text{NaOH} &:: \frac{1}{142\cdot6} : \frac{562}{40} = 701 : 1405 \\ &= 1 : 2 \end{aligned}$$

or one molecule of Cu_2O liberates two molecules of sodium hydrate according to the following equation:—



The cuprous thiosulphate is kept in solution by the excess of sodium thiosulphate. This solution is very unstable under ordinary circumstances and black copper sulphide soon separates out. Here we have the explanation of the formation of the black sulphide when the yellow salt is treated with caustic soda. The reaction may therefore be represented by the following equation:—



During the first stage of the reaction the whole of the copper is obtained as cuprous oxide, but the bright redish yellow cuprous oxide being in contact with an excess of sodium thiosulphate in course of time gradually darkens in colour and quite rapidly on heating as the result of the other equation stated above, and subsequent conversion of the cuprous thiosulphate into copper sulphide. It is for this reason again copper cannot be precipitated as oxide by means of caustic soda from a solution containing one mol. of copper sulphate to two or more molecules of sodium thiosulphate. Here we have also the explanation

of the little discrepancy noticed between the thiosulphuric acid determined by direct titration (method B) and that obtained from the total sulphur calculated as thiosulphuric acid.

The yellow salt described before dissolves easily in dilute hydrochloric acid without any apparent change. Concentrated hydrochloric acid on the other hand precipitates a white crystalline salt which settles down at once. After a while, however, sulphur dioxide is given off freely from both, and the supernatant liquid turns brown. The white salt if washed immediately with a little water and finally with alcohol is a rather stable one. It can in fact be heated in steam chamber without decomposition. In contact with the mother liquor containing strong hydrochloric acid it decomposes so soon that the washing of the salt becomes difficult and at times impracticable. Besides in presence of a large quantity of strong hydrochloric acid a proportionally large quantity of sodium chloride is precipitated and cannot therefore be completely removed by alcohol. If instead of hydrochloric acid, acetic acid be used, sodium acetate is formed and can be easily removed by washing and filtration with dilute alcohol in which menstruum it is rather freely soluble. We accordingly prepared at first a saturated solution of copper chloride in dilute acetic acid and then gradually added to it a strong solution of sodium thiosulphate, when a perfectly white salt was precipitated. Subsequent experience proved that even acetic acid is not necessary, and the white salt is obtained when a strong solution of sodium thiosulphate is gradually added to an equally strong solution of copper chloride. The precipitate is obtained in fine impalpable powder which settles down easily and can therefore be filtered and washed without any considerable difficulty. The result of the analysis of the different samples is given in the annexed table. From the mean atomic ratio $\text{Cu} : \text{Na} : \text{S} : \text{Cl} : \text{O} : \text{H}_2\text{O} = 3 : 3.01 : 4.68 : 1.29 : 10.78 : 1.91$ the salt with the formula $9 \text{Cu}_2\text{S}_2\text{O}_3 \cdot 5 \text{Na}_2\text{S}_2\text{O}_3 \cdot 8 \text{NaCl} \cdot 12 \text{H}_2\text{O}$ is obtained having the following percentage composition:—

$\text{Cu} = 31.46$	$\text{S} = 24.78$	$\text{O} = 28.76$
$\text{Na} = 11.45$	$\text{Cl} = 7.85$	$\text{H}_2\text{O} = 5.97$

If strong solutions of copper sulphate or acetate and sodium thiosulphate be mixed nearly in the proportion of one molecule of the former to two molecules of the latter and allowed to remain for some time as in other cases, no yellow salt separates out. If on the other hand a large excess of concentrated acetic acid be added to the mixture a white or faintly yellowish white precipitate is obtained which is more soluble in water than the yellow salt. Copper acetate should therefore be used in preference to copper sulphate. It can then be washed with

dilute alcohol instead of with water until free from sodium acetate and finished as before. It appears as probable that the acetic acid plays the same part in this case as alcohol does in Vortmann's salts. The white or faintly yellowish white salt turns yellow in contact with water especially if the salt be previously dried. On comparison of the result of analysis of the different preparations as given in the annexed table we find that this salt again is a double thiosulphate of copper and sodium having the formula $\text{Cu}_2\text{S}_2\text{O}_3 \text{Na}_2\text{S}_2\text{O}_3 \cdot 2\frac{1}{2} \text{H}_2\text{O}$. Russel describes (Ch. Ztg. 9233) a salt $\text{Cu}_2\text{S}_2\text{O}_3 \text{Na}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ whose properties and method of preparation are altogether different from the one described here. This salt when once perfectly dry, also keeps well even in contact with the atmosphere.

Table of analysis of the white salt obtained by the action

DATE.	Sample.	Weight in grams of substance used.	Weight in grams of Cu_2S .	Weight in grams of N_2SO_4 .	Weight in grams of BaSO_4 .	Weight in grams of Ag Cl.	Weight in grams of Ag Br.	Weight in grams of H_2O .
Jan. 14, 1897...	D. 1.	0·214	0·3898
		0·3235	0·1281	0·1175
	D. 2.	0·3371	0·1402	...	0·6296
		0·2220	0·0798	0·061
	D. 3.	1·1468	0·4592	0·4036
		0·7384	1·3463
		0·8804	0·3516
		0·4602	3·1193	...
		0·5071	0·1527
		1·6106	0·0931
		D. 4.	0·9890	0·3869	0·3541
	0·4552		3·042	...
	0·8380		1·5119
	0·7392		0·2352
	1·5640		0·6160	0·5574	0·0909
	1·5015		0·0895

of hydrochloric acid (concentrated) on the yellow salt.

PERCENTAGE OF						ATOMIC RATIO OF						REMARKS.
Cu.	Na.	S.	Cl.	O.	H ₂ O.	Cu.	Na.	S.	Cl.	O.	H ₂ O	
...	...	25.05	The yellow salt was dissolved in dilute hydrochloric acid and then precipitated by strong hydrochloric acid and washed with alcohol.
31.53	11.75	3.00	3.06	4.7	
32.99	...	25.65	The result is high owing to the salt being slightly decomposed.
32.2	6.8	
32.08	11.4	}	Deducting the weight of Ag Cl.
...	...	25.06	
32.09	}	3.0	2.93	4.63	1.24	10.77	1.9
...	28.86
...	7.45	}
...	5.78
31.19	11.6	}	Perfectly white sample. Deducting the weight of Ag Cl.
...	28.45	...		3.0	3.05	4.7	1.34	10.78	
...	...	24.8	}
...	7.87
31.43	11.55	5.81
...	5.96
					Mean	3.0	3.01	4.68	1.29	10.78	1.91	

*Table of analysis of salt obtained by the addition of strong acetic acid to a mixture of sodium
Thiosulphate and copper acetate solutions.*

REMARKS.	ATOMIC RATIO OF														
	H ₂ O	O.	S.	Na.	Cu.	Cu.	Na.	S.	O.	H ₂ O					
		PERCENTAGE OF													

The little discrepancy in the atomic ratio was due to the presence of a small quantity of sodium salt washed out.